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C—H···O Packing Motifs in Some Cyclopenta[*a*]phenanthrenes

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Abstract

An analysis has been made of the C—H···O interactions in cyclopenta[*a*]phenanthrenes, for which structural data on fifteen 15,16-dihydrocyclopenta[*a*]-phenanthren-17-ones are available. These compounds mostly contain only one O atom, a carbonyl group at the 17-position, and therefore the only groups available for interactions are C—H groups. In addition, the crystal structure of a second polymorph of the 11-ethyl derivative is described. M_r = 260.33, *Pbca*, a = 17.012 (2), b = 21.042 (2), c = 7.6465 (6) Å, V = 2737.2 (4) Å^3, Z = 8, D_x = 1.264 Mg m^{-3}, Cu $K\alpha$, λ = 1.5418 Å, μ = 0.56 mm^{-1}, $F(000)$ = 1104, T = 295 K, final R = 0.090 for 1669 reflections above $2\sigma(F)$. The conformation of the ethyl group is *gauche* [C(12)—C(11)—C(18)—C(19) = 75.8 (7)°], differing from the *cis* value of −1.3 (5)° for the *Pnaa* form. The molecular distortion in the *Pbca* polymorph is also larger than that in the *Pnaa* polymorph; this distortion is evidenced by torsion angles (13–20°) in the bay region and by an out-of-plane displacement (0.8 Å) of the C atom of the methylene portion of the ethyl group [the C atom attached to C(11)]. Packing diagrams and intermolecular distances were analyzed for all the dihydrocyclopenta[*a*]phenanthrenes for which structural data are available. There appear to be three types of packing. The first type consists of a dimer herringbone formed by the interactions of two molecules by way of the ketone group and the C—H of C(12) of the adjacent ring. The second type of packing also involves a dimer but involves C—H and O=C groups at either ends of the molecule. The third type is a layer structure and involves com-

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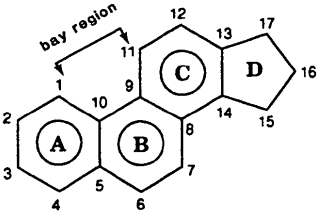
pounds that crystallize with a unit-cell length of 7.5–7.6 Å (or, in a very planar structure, 13.8 Å). The translational stacking (~4 Å apart) found in polycyclic aromatic hydrocarbons is not observed in the crystal structures of these dihydrocyclopenta[*a*]-phenanthrenes because of the bulk of methyl or methylene groups and the dipole moment of the carbonyl group.

Introduction

The dihydrocyclopenta[*a*]phenanthrenes are polycyclic compounds with chemical formulae [shown in (I)] that resemble those of the steroids (so that the same numbering system is used) as well as those of the carcinogenic polycyclic aromatic hydrocarbons (PAHs). Atoms C(1), C(10), C(9) and C(11) constitute the 'bay region', the active area in carcinogenesis by PAHs. Since the structural similarities between steroids, carcinogenic PAHs and nucleic acid–base pairs have been noted (Haddow, 1957; Huggins & Yang, 1962), it is not surprising that some of the substituted derivatives of 15,16-dihydrocyclopenta[*a*]phenanthren-17-one are carcinogenic (Coombs & Croft, 1969; Coombs, Jaitly & Crawley, 1970). The crystal structures of 13 such 15,16-dihydrocyclopenta[*a*]phenanthren-17-one derivatives have been determined by X-ray diffraction methods (Clayton, Coombs, Henrick, McPartlin & Trotter, 1983; Kashino, Zacharias, Peck, Glusker, Bhatt & Coombs, 1986) and the bay-region distortions caused by substitution mimic those found for the analogous PAHs.



(I)

Unlike the PAHs, which contain only C and H atoms, the 15,16-dihydrocyclopenta[*a*]phenanthren-17-ones have one carbonyl oxygen attached to the ring system. Therefore they provide an excellent subject for analyzing perturbations in the packing arrangements in crystalline PAHs (Kitaigorodsky, 1973) as a result of the presence of such an oxygen-containing functional group. Hydrogen bonding generally aids in efficient packing of molecules in a crystal, but is not possible for the dihydrocyclopentaphenanthrenes because no —OH or —NH groups are present that can donate an H atom to a hydrogen bond. Therefore intermolecular C—H···O hydrogen bonding (Sutor, 1963; Donohue, 1968), although weaker than O—H···O or N—H···O hydrogen bonding, might be predicted to occur between the C—H groups and the O atom of the keto group. Even a small stoichiometry of oxygen in a PAH would be expected to have a significant effect on the mode of packing in crystals if such interactions occur. The aim here is to investigate these effects.

We present here data on the crystal structure of an additional dihydrocyclopenta[*a*]phenanthrene derivative, a polymorph of one previously studied. We then present an analysis of the packing motifs found in such structures, and compare them with those found for PAHs lacking any functional oxygen substitution (Robertson, 1951; Gavezzotti & Desiraju, 1988).

Experimental

During a structural study of 15,16-dihydro-17-oxocyclopenta[*a*]phenanthrenes (Kashino *et al.*, 1986) it was found that crystals of the 11-ethyl derivative had a tendency to grow as twins of the *Pbca* and *Pnaa* forms. The structure of the *Pnaa* form has already been determined by use of a single crystal (Kashino *et al.*, 1986). In the present work the structure of the *Pbca* polymorph has been determined. Distortions in the bay region are compared with those in molecules in the *Pnaa* form where the crystallographic environment of the molecules is different.

A crystal of the *Pbca* form was obtained by cutting a large twinned crystal (containing both polymorphs). The crystal was elongated along the *c* axis and had dimensions 0.20 × 0.08 × 0.45 mm. Lattice parameters were determined by least-squares methods, from measurements on 20 reflections. A Rigaku AFC-5 four-circle diffractometer was used for intensity data measurement. Intensities were measured up to $2\theta = 125°$ by the ω–2θ scan method, scan speed 4° min^{-1} in 2θ, scan range $(1.2 + 0.35\tan\theta)°$. The X-radiation used was Ni-filtered Cu $K\alpha$ at 40 kV and 200 mA. Background intensities were measured for 4 s on either side of the peak. Three reference reflections showed no intensity deterioration during the data collection. Intensities were corrected for Lorentz and polarization factors, but not for absorption. There were 2180 independent reflections in the measured data set and of these 1669 reflections (ranging over $h = 0$ to 19, $k = 0$ to 24, $l = 0$ to 8) with $|F_o| > 2\sigma(F)$ were used in the structure refinement. The strongest reflection, 002, was affected by secondary extinction ($F_o = 305.7$, $F_c = 438.5$) and was therefore omitted from the refinement.

The structure was solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), and refined by full-matrix least squares. Atomic scattering factors were taken from *Inter-*

national Tables for X-ray Crystallography (1974, Vol. IV, pp. 72–73). H-atom scattering factors were those listed by Stewart, Davidson & Simpson (1965). The quantity minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, with $w = 1.0/[\sigma(F)^2 + 0.0657|F_o| + 0.0018|F_o|^2]$. Locations of H atoms were determined from a difference Fourier synthesis, refined by least squares, except for H(193), whose positional parameters were fixed at the idealized position with $B_{iso} = 10.0$ Å^2. In the final refinement cycle $wR = 0.132$, $S = 1.19$ and values of $(\Delta/\sigma)_{max}$ were 0.1 for non-H atoms and 0.2 for H atoms. The maximum peak height, $\Delta\rho$, in the final difference Fourier map was 0.42 e Å^{-3} and the minimum $\Delta\rho$ was -0.19 e Å^{-3}. The high value of $\Delta\rho_{max}$ suggested some kind of disorder in the ethyl group, but it was not possible to derive a reasonable model for this disorder based on either Fourier or difference Fourier maps. Therefore, the refinement was terminated ($R = 0.090$). Computations were carried out at the Crystallographic Research Center, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center; programs used were *MULTAN*78 (Main *et al.*, 1978), *FMLS* and *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979) and *ORTEP* (Johnson, 1965).

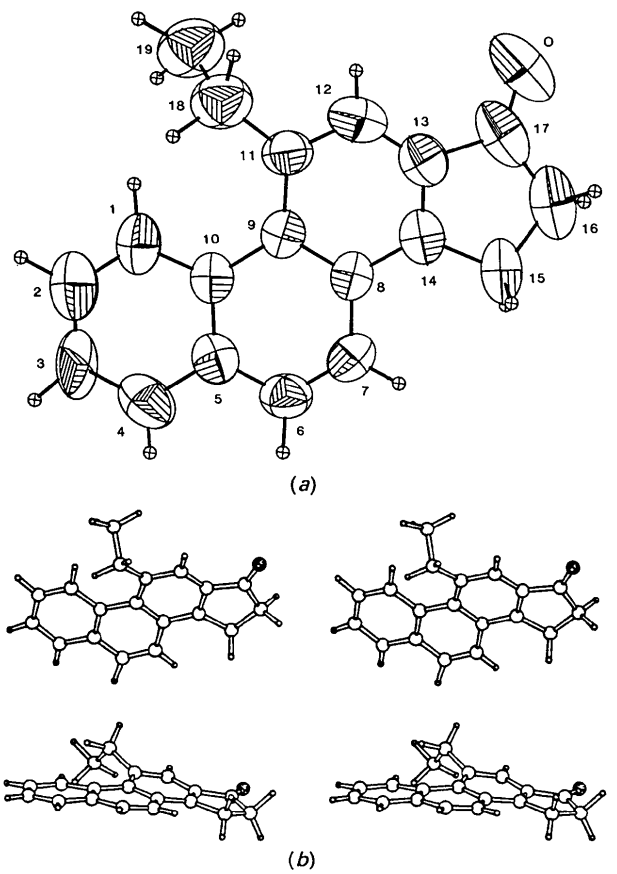


Fig. 1. (*a*) Thermal ellipsoid (50% probability) representation (Johnson, 1965) of the *Pbca* polymorph of the 11-ethyl derivative showing atomic numbering. (*b*) Stereoviews of the molecule. O atom stippled. H atoms small circles.

Table 1. *Final atomic parameters with e.s.d. values in parentheses*

$B_{eq} = (4/3)\sum_i\beta_{ii}/a_i^{*2}$.

	x	*y*	*z*	B_{eq}, B_{iso} (Å^2)
O	0.5455 (3)	0.4174 (2)	0.1326 (6)	10.8 (3)
C(1)	0.4181 (3)	0.0808 (2)	0.0864 (6)	6.9 (2)
C(2)	0.3832 (4)	0.0229 (2)	0.0815 (8)	8.5 (4)
C(3)	0.3061 (4)	0.0166 (2)	0.0269 (8)	9.2 (4)
C(4)	0.2642 (3)	0.0694 (3)	−0.0252 (7)	7.7 (3)
C(5)	0.2992 (3)	0.1300 (2)	−0.0212 (5)	5.5 (2)
C(6)	0.2546 (2)	0.1844 (2)	−0.0626 (6)	6.3 (2)
C(7)	0.2835 (3)	0.2424 (2)	−0.0440 (6)	5.9 (2)
C(8)	0.3634 (2)	0.2522 (2)	0.0108 (5)	4.9 (2)
C(9)	0.4144 (2)	0.2001 (2)	0.0357 (5)	5.0 (2)
C(10)	0.3790 (3)	0.1364 (2)	0.0309 (5)	5.1 (2)
C(11)	0.4965 (3)	0.2129 (2)	0.0624 (6)	6.2 (2)
C(12)	0.5189 (3)	0.2749 (3)	0.0886 (7)	7.3 (2)
C(13)	0.4671 (3)	0.3250 (2)	0.0798 (6)	6.2 (2)
C(14)	0.3915 (3)	0.3149 (2)	0.0350 (5)	5.5 (2)
C(15)	0.3466 (3)	0.3766 (2)	0.0172 (6)	7.0 (2)
C(16)	0.4049 (4)	0.4273 (2)	0.0716 (7)	8.5 (3)
C(17)	0.4816 (4)	0.3935 (3)	0.0989 (6)	7.9 (3)
C(18)	0.5637 (3)	0.1640 (3)	0.0340 (8)	8.8 (3)
C(19)	0.6060 (4)	0.1463 (3)	0.1950 (8)	9.9 (4)
H(1)	0.477 (3)	0.084 (2)	0.128 (7)	8 (1)
H(2)	0.415 (4)	−0.017 (4)	0.127 (11)	15 (2)
H(3)	0.275 (2)	−0.022 (2)	0.018 (5)	6 (1)
H(4)	0.213 (2)	0.066 (2)	−0.060 (5)	3.3 (8)
H(6)	0.202 (2)	0.175 (2)	−0.118 (5)	4.7 (9)
H(7)	0.253 (2)	0.279 (2)	−0.076 (5)	3.5 (8)
H(12)	0.569 (2)	0.279 (2)	0.108 (7)	6 (1)
H(151)	0.301 (2)	0.377 (2)	0.092 (5)	4.4 (9)
H(152)	0.327 (3)	0.380 (2)	−0.115 (6)	7 (1)
H(161)	0.388 (2)	0.454 (2)	0.183 (5)	6 (1)
H(162)	0.424 (3)	0.462 (3)	−0.038 (7)	10 (2)
H(181)	0.539 (3)	0.120 (3)	−0.012 (8)	9 (2)
H(182)	0.619 (4)	0.178 (3)	−0.031 (8)	9 (1)
H(191)	0.621 (3)	0.189 (3)	0.268 (8)	10 (2)
H(192)	0.650 (3)	0.106 (3)	0.151 (8)	9 (1)
H(193)	0.569	0.116	0.274	10

Discussion

Description of the crystal structure

The thermal ellipsoids of the molecule are shown in Fig. 1(*a*) and a stereoview of the molecule is given in Fig. 1(*b*). The ellipsoids of the non-H atoms in rings *A*, *D* and the ethyl group are fairly large, and suggest that there may also be some disorder in these atoms. The refined atomic parameters are listed in Table 1 and bond lengths are given in Table 2.*

The molecular dimensions and conformations in the *Pbca* and *Pnaa* forms of the 11-ethyl derivatives

* Lists of anisotropic thermal parameters, torsion angles, C—H bond distances and angles, non-bonded intermolecular distances, atomic coordinates used in calculating Table 5, structure factors, and parameters for anisotropic atoms with principal axes and their direction cosines which define the thermal ellipsoids have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55994 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0438]

Table 2. *Bond lengths* (Å) *and interbond angles* (°)

	Pbca form (XIII)	*Pnaa* form (XII)	(XIII) − (XII)
C(1)—C(2)	1.356 (9)	1.354 (4)	0.00
C(2)—C(3)	1.383 (11)	1.403 (5)	−0.02
C(3)—C(4)	1.379 (10)	1.343 (4)	0.04
C(4)—C(5)	1.408 (7)	1.423 (4)	−0.02
C(5)—C(6)	1.409 (6)	1.439 (4)	−0.03
C(5)—C(10)	1.421 (6)	1.402 (4)	0.02
C(6)—C(7)	1.323 (7)	1.320 (4)	0.00
C(7)—C(8)	1.437 (6)	1.438 (3)	−0.00
C(8)—C(9)	1.411 (6)	1.414 (4)	−0.00
C(8)—C(14)	1.415 (6)	1.405 (4)	0.01
C(9)—C(10)	1.470 (6)	1.475 (3)	−0.01
C(10)—C(1)	1.411 (6)	1.423 (4)	−0.01
C(9)—C(11)	1.437 (6)	1.441 (4)	−0.00
C(11)—C(12)	1.374 (8)	1.385 (4)	−0.01
C(12)—C(13)	1.376 (8)	1.404 (4)	−0.03
C(13)—C(14)	1.348 (7)	1.360 (4)	−0.01
C(14)—C(15)	1.512 (7)	1.530 (3)	−0.02
C(15)—C(16)	1.515 (9)	1.558 (4)	−0.04
C(16)—C(17)	1.501 (10)	1.496 (5)	0.01
C(17)—C(13)	1.470 (9)	1.468 (4)	0.00
C(17)—O	1.225 (9)	1.211 (4)	0.01
C(11)—C(18)	1.553 (8)	1.537 (4)	0.02
C(18)—C(19)	1.474 (8)	1.460 (4)	0.01
C(1)—C(2)—C(3)	120.7 (6)	121.4 (3)	−0.7
C(2)—C(3)—C(4)	120.0 (7)	118.3 (3)	1.7
C(3)—C(4)—C(5)	120.3 (6)	121.8 (3)	−1.5
C(4)—C(5)—C(10)	119.7 (4)	120.5 (2)	−0.8
C(5)—C(10)—C(1)	117.1 (4)	115.8 (2)	1.3
C(10)—C(1)—C(2)	122.0 (5)	122.2 (2)	−0.2
C(4)—C(5)—C(6)	120.2 (4)	118.5 (2)	1.7
C(5)—C(6)—C(7)	121.7 (5)	120.6 (2)	1.1
C(6)—C(7)—C(8)	121.0 (5)	120.7 (2)	0.3
C(7)—C(8)—C(9)	120.6 (4)	122.1 (2)	−1.5
C(8)—C(9)—C(10)	117.0 (4)	116.3 (2)	0.7
C(9)—C(10)—C(5)	119.0 (4)	119.2 (2)	−0.2
C(10)—C(5)—C(6)	120.0 (4)	121.0 (2)	−1.0
C(1)—C(10)—C(9)	123.7 (4)	124.9 (2)	−1.2
C(7)—C(8)—C(14)	119.4 (4)	117.2 (2)	2.2
C(8)—C(9)—C(11)	118.1 (4)	118.9 (2)	−0.8
C(9)—C(11)—C(12)	117.9 (5)	118.0 (2)	−0.1
C(11)—C(12)—C(13)	122.9 (5)	121.9 (3)	1.0
C(12)—C(13)—C(14)	120.2 (5)	120.6 (3)	−0.4
C(13)—C(14)—C(8)	120.2 (5)	119.8 (2)	0.4
C(14)—C(8)—C(9)	119.9 (4)	120.7 (2)	−0.8
C(10)—C(9)—C(11)	124.9 (4)	124.8 (2)	0.1
C(9)—C(11)—C(18)	124.8 (4)	124.0 (2)	0.8
C(18)—C(11)—C(12)	116.4 (5)	118.0 (2)	−1.6
C(13)—C(14)—C(15)	111.7 (4)	111.6 (2)	0.1
C(14)—C(15)—C(16)	104.4 (4)	103.1 (2)	1.3
C(15)—C(16)—C(17)	105.9 (5)	106.4 (2)	−0.5
C(16)—C(17)—C(13)	107.8 (6)	107.9 (3)	−0.1
C(17)—C(13)—C(14)	109.9 (5)	110.8 (3)	−0.9
C(12)—C(13)—C(17)	129.7 (5)	128.6 (3)	1.1
C(13)—C(17)—O	124.9 (6)	126.5 (3)	−1.6
O—C(17)—C(16)	127.3 (6)	125.6 (3)	1.7
C(8)—C(14)—C(15)	128.2 (4)	128.5 (2)	−0.3
C(11)—C(18)—C(19)	114.2 (5)	117.1 (3)	−2.9

are compared in Tables 2 and 3. Differences in bond length are probably not significant in view of the thermal motion observed. The ethyl group adopts the *gauche* conformation in the *Pbca* form, while it is in a *cis* conformation in the *Pnaa* form. As a result, the steric hindrance between the methylene H atoms and C(1) is larger in the *Pbca* form [H(181)···H(1) 1.68 Å] than in the *Pnaa* form (where this distance is 1.84 Å). The molecular distortion is evidenced (as shown in Table 3) by the torsion angles C(10)—C(9)—C(11)—C(18) and C(1)—C(10)—C(9)—C(11) in the bay region, the planarity of the rings *B* and *C*, the dihedral angles between rings *B* and *C* and between *A* and *C*, and the deviation of C(18) from the least-squares plane C(1) through C(17). The influence on the interbond angles, however, is small.

Table 3. *Comparison of the molecular conformations in Pbca form* (2) (XIII) (*this work*) *and Pnaa form* (1) (XII) *of* 11-*ethylcyclopenta*[*a*]*phenanthrene*-17-*one*

Root-mean-square deviations (Å) of the ring planes

	Rings *A*	*B*	*C*	*D*
Form (2)	0.011 (7)	0.035 (5)	0.036 (6)	0.026 (7)
Form (1)	0.011 (4)	0.018 (4)	0.016 (4)	0.024 (4)

Dihedral angles (°) between rings

	Rings *A*/*B*	*B*/*C*	*C*/*D*	*A*/*C*	*B*/*D*	*A*/*D*
Form (2)	6.2 (2)	7.2 (2)	3.0 (2)	13.3 (2)	6.9 (2)	13.1 (2)
Form (1)	4.0 (2)	3.8 (2)	1.9 (2)	7.3 (1)	1.9 (2)	5.5 (2)

Maximum deviations (Å) and deviation (Å) of C(18) from the plane through rings *A*, *B*, *C* and *D*

	Maximum deviations	Deviation of C(18)
Form (2)	0.278 (8) at C(16) −0.294 (6) at C(11)	−0.820 (7)
Form (1)	0.134 (3) at C(2) −0.126 (3) at C(11)	−0.308 (5)

Torsion angles (°)

	12–11–18–19	10–9–11–18	1–10–9–11	7–8–14–15
Form (2) (*gauche*)	75.8 (7)	19.8 (7)	13.3 (7)	2.6 (7)
Form (1) (*cis*)	−1.3 (5)	4.4 (5)	8.9 (5)	1.2 (5)

Bond angles (°) in bay region

	9–11–18	11–9–10	1–10–9	18–11–12
Form (2)	124.8 (4)	124.9 (4)	123.7 (4)	116.4 (5)
Form (1)	124.0 (2)	124.8 (2)	124.9 (2)	118.0 (2)

It is apparent that the molecular conformation of the 11-ethyl derivative is affected by the conformation of the substituent in the bay region and that the steric hindrance in cyclopenta[*a*]phenanthrenes can be relieved by out-of-plane distortions as well as in-plane distortions.

Description of packing in this structure

In the crystal structure, molecules related by a *b*-glide plane, a center of symmetry and a twofold screw axis along the **a** direction are hexagonally packed to form a sheet parallel to (001). The molecular arrangement in the sheet is very similar to that in the *Pnaa* form. The molecules related by a *c*-glide plane are stacked along the **c** direction with a dihedral angle of 2.7 (1)°. If the dihedral angle were 0°, the glide plane would be reduced to a twofold axis, which is found in the *Pnaa* form. There are C=O···H—C interactions between the molecules related by a twofold screw axis along the **b** direction [O···C 3.344 (9), O···H 2.40 (8) Å, O···H—C 149 (6)°]. The formation of the twinned crystals is reasonably explained by the similarity of the two crystal structures, as shown in Fig. 2.

Comparisons of structures of cyclopentaphenanthrene derivatives

Geometrical data on the 15 different crystal structures, listed in Table 4, were compared in terms of molecular conformation and packing modes. Their

formulae are given in Fig. 3. The molecules contain flat aromatic rings *A*, *B* and *C*. The C atoms of the cyclopentanone ring (*D*) lie in a plane with the methylene H atoms eclipsed. Examples of the planarities of molecules are illustrated in Figs. 1 and 4. The most distorted molecule (apart from the 11-methyl-11,12-dihydro derivative which is quite different from the other structures described here) is the 7,11-dimethyl derivative (Kashino *et al.*, 1986). Substitution by a methyl group in the 11-position causes overcrowding in the bay region [between C(1) and C(11)]. In-plane distortions that occur to alleviate this effect increase, to some extent, any overcrowding in the area between C(7) and C(15). A second substitution in the 7-position removes any possibility of such a compensation by in-plane distortions. Therefore, out-of-plane molecular distortions occur in a manner similar to those found in the carcinogen 7,12-dimethylbenz[*a*]anthracene (Klein, Stevens, Zacharias & Glusker, 1987). The effect of methylation in the 6-position is to cause overcrowding in the quasi-bay region [C(7)—C(15)] and therefore it is not surprising that the C(1)···C(11) distance is the smallest (2.935 Å) found in this group of compounds.

The exception to the effect of atomic overcrowding by substitution in the bay region is provided by the 11-MeO derivative which is essentially planar (Kashino *et al.*, 1986). The C(1)···C(11) distance is similar (3.084 Å) to those found in the other compounds not substituted in the 11-position (2.935–3.118 Å) and the planarity of the 11-OMe derivative, shown in Fig. 4, is possibly the result of an intermolecular C—H···O interaction. The nonbonded C(19)···O(2) distance is 2.708 Å which is 0.25 Å smaller than any with a C atom in place of the methoxy O atom. While it is always difficult to establish criteria for intramolecular interactions, especially weak ones like C—H···O bonds, this shortening of the intramolecular distance by such a large amount with concomitant lack of distortions in the planarity or in the bay-region angles can well be

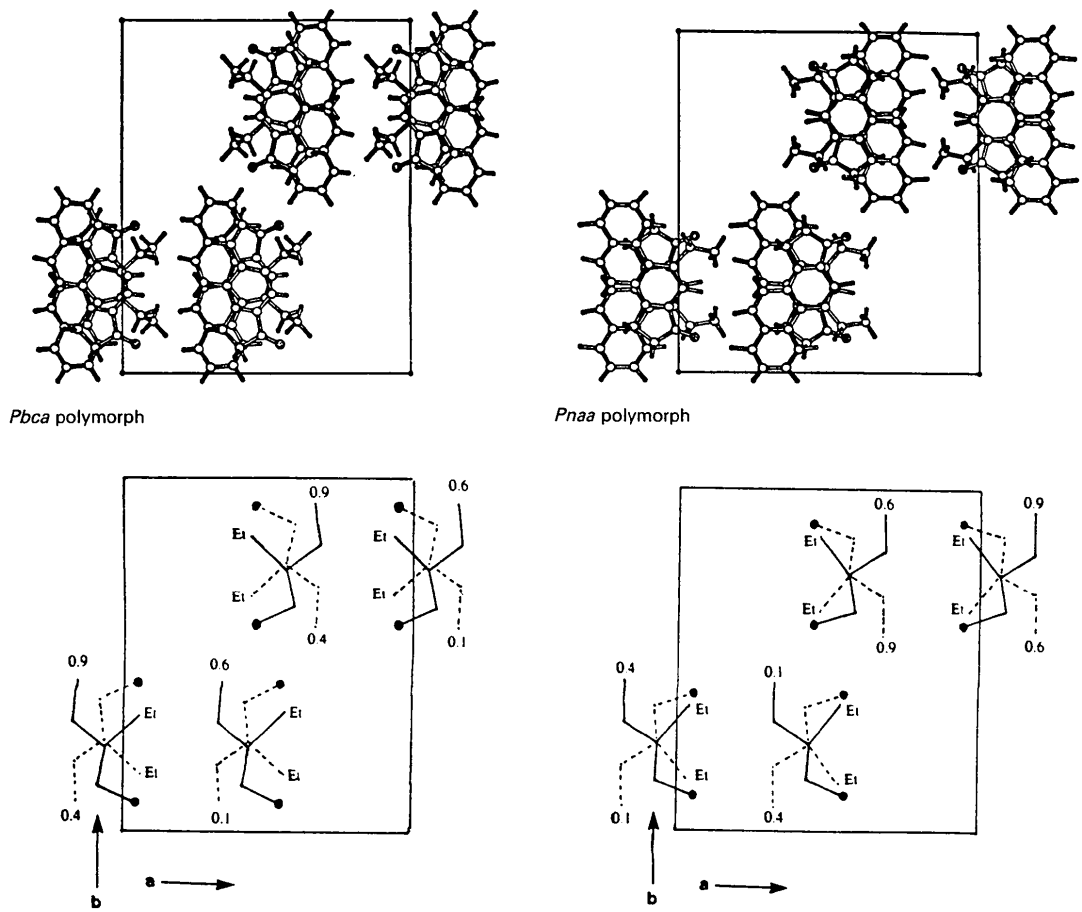


Fig. 2. Comparison of packing in the crystal structures of the *Pbca* (left) and *Pnaa* (right) polymorphs of the 11-ethyl derivative. Above is shown the packing of eight molecules. Below is a diagram illustrating this – O atoms black filled circles. The centers of rings and locations of ketone oxygen and one ethyl C atom are shown. Approximate heights along the *c* axis are indicated in this diagram.

significant with respect to such an intramolecular hydrogen bond.

C—H···O *interactions*

Weak C—H···O interactions help to form networks of molecules and they may be classified into one of two types:

(*a*) a linear arrangement shown in Fig. 5(*a*) or

(*b*) a branched arrangement shown in Figs. 5(*b*) and 5(*c*) where two or more C—H groups interact with the carbonyl O atom. These may lie in the plane of the carbonyl group (Fig. 5*b*) or one of the groups may be out of the carbonyl plane as shown in Fig. 5(*c*).

Bonds of the variety (*b*) may be preferred here since there are a large number of potential donor C—H groups for each O atom. The angular preferences for the C—H···O contacts correspond to familiar patterns and have been described previously (Taylor & Kennard, 1982; Desiraju, 1989) with bonding C—H···O angles near 180° and C=O···H angles near 120°. Some examples of C—H surroundings of the carbonyl group are shown in Fig. 6(*a*)

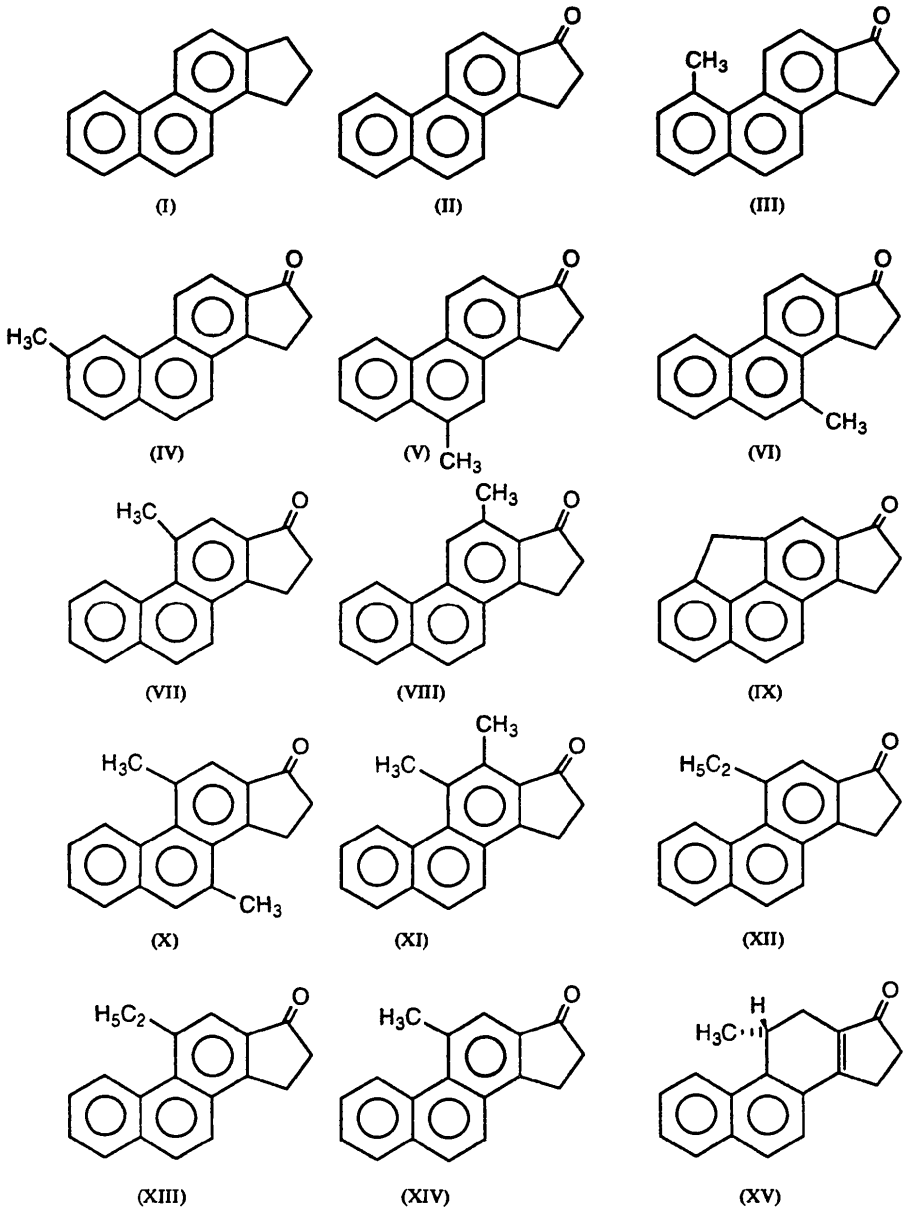


Fig. 3. Formulae of the compounds described.

Table 4. *Crystal data for the* 13 *cyclopenta[a]phenanthrenes shown in Fig.* 3

Compound	No C=O	Unsubstituted	1-Me	2-Me	6-Me	7-Me	11-Me	12-Me
Crystal data	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
Formula	$C_{17}H_{14}$	$C_{17}H_{12}O$	$C_{18}H_{14}O$	$C_{18}H_{14}O$	$C_{18}H_{14}O$	$C_{18}H_{14}O$	$C_{18}H_{14}O$	$C_{18}H_{14}O$
M_r		232.28	246.31	246.31	246.31	246.31	246.31	246.31
M.p. (°C)		203–204	189–190	221–222	210.5–212	198–199	171–172	233
Space group	$P2_1/a$	$P2_1/c$	*Pbca*	$P2_1/c$	$P2_1/c$	$P2_1/c$	*Pcab*	*Pbca*
a (Å)	18.350	10.243	14.344	11.965	7.587	7.562	14.355	9.746
b (Å)	5.869	5.445	23.121	9.867	7.777	12.532	23.153	12.231
c (Å)	11.610	20.642	7.571	10.749	21.122	13.490	7.526	20.882
β (°)	111.61	109.20	90	93.71	100.98	92.97	90	90
V (Å^3)		1087.2	2510.9	1263.6	1223.4	1275.8	2488.5	2489.2
D_x (g cm^{-3})		1.419	1.303	1.294	1.337	1.282	1.308	1.314
Z	4	4	8	4	4	4	8	8
Final R	0.10	0.083	0.052	0.084	0.058	0.081	0.051	0.071
Structure type		1	3	2	3	3	3	2
Rings *A/D*								
Dihedral angle (°)	2.6	1.6	3.3	6.3	1.7	3.2	11.9*	1.9

Compound	7,11-diMe	11,12-diMe	11-Et	11-Et (this work)	11-OMe	1,11-CH_2	11-Me-11,12-H_2
Crystal data	(X)	(XI)	(XII)	(XIII)	(XIV)	(IX)	(XV)
Formula	$C_{19}H_{16}O$	$C_{19}H_{16}O$	$C_{19}H_{16}O$	$C_{19}H_{16}O$	$C_{18}H_{14}O_2$	$C_{18}H_{12}O$	$C_{18}H_{16}O$
M_r	260.33	260.33	260.33	260.33	262.31	244.30	248.32
M.p. (°C)	208–210	149–150	129–130		179	195	177–178
Space group	$P2_1cn$	$P2_1/n$	*Pnaa*	*Pbca*	*Fddd*	*Pcab*	$P2_1/n$
a (Å)	11.640	20.368	17.820	17.012	21.567	7.504	12.743
b (Å)	15.131	5.751	20.365	21.042	35.192	15.093	8.781
c (Å)	7.531	11.494	7.584	7.646	13.823	21.869	11.721
β (°)	90	90.68	90	90	90	90	95.92
V (Å^3)	1326.3	1346.5	2752.3	2737.2	10491	2464.3	1304.5
D_x (g cm^{-3})	1.304	1.284	1.257	1.264	1.329	1.316	1.264
Z	4	4	8	8	32	8	4
Final R value	0.056	0.059	0.070	0.090	0.056	0.081	0.063
Structure type	3	1	3	3	3?	3	
Rings *A/D*							
Dihedral angle (°)	20.6	12.7	5.5	13.1	3.4	3.7	10.5

* Corrected value.

and the scatterplot, which is wide, is shown in Fig. 6(*b*). Some of the shorter contacts are illustrated in Fig. 6(*c*).

Comparison of packing modes in cyclopenta[a]-phenanthren-17-one derivatives

There is only one (rarely two) O atom(s) in these molecules, but the effects of the O atoms are evident in the C—H···O interactions. While the parent molecule (I) (with no oxygen in the molecule) is nonpolar and adopts a close-packed crystal structure, the C—H···O hydrogen bonds may be considered as determinants of the crystal structures of the oxygenated derivatives (II)–(XV) studied here. All but one of the 14 crystal structures we discuss here are centrosymmetric and none are triclinic. The reasons for these preferences will become apparent in the following discussion.

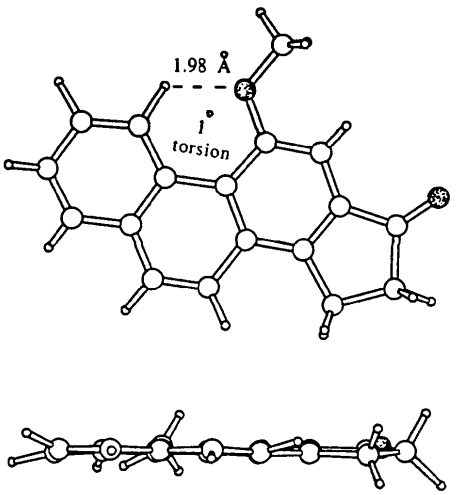


Fig. 4. 11-Methoxy derivative showing the planarity of the molecule and the short C—H···O intramolecular interaction.

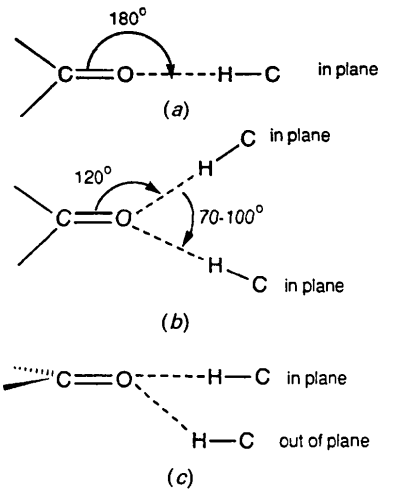


Fig. 5. (*a*)–(*c*) Types of C—H···O interactions.

The association of molecules to form crystals is effected by the C—H···O interactions (documented in Table 5) and these types of associations can be roughly divided into three structural classifications. The first structural type, which is seen in the structure of the unsubstituted (II) and 11,12-diMe (XI) compounds, consists of centrosymmetric C—H···O bonded dimers which are themselves packed in a herringbone pattern characterized by a short axis 5.44 and 5.75 Å, respectively. While the hydrogen-

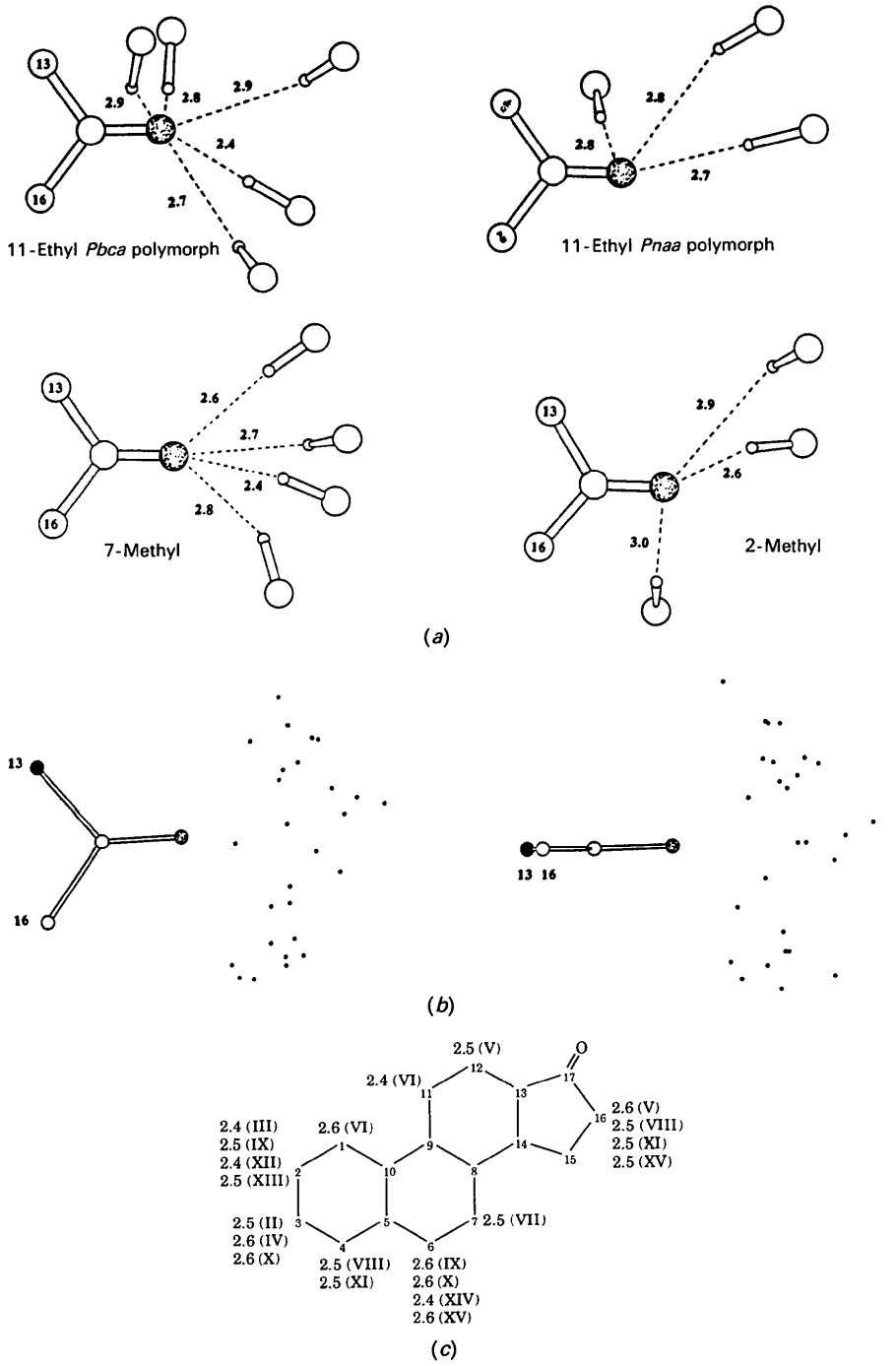


Fig. 6. Packing of C—H groups around the ketone O atoms. (*a*) Plots for a selection of compounds. (*b*) Plots onto C=O plane and along it for all interactions with H···O less than 2.7 Å. (*c*) Carbonyl groups that approach —C—H groups with the distance in Å and the compound (as listed in Fig. 3). Positions 2, 6 and 16 have most H···O interactions less than 2.7 Å.

Table 5. *Geometry of* C—H···O *interactions*

Hydrocarbon (I)		C—H* (Å)	O···H (Å)	O···C (Å)	O···H—C (°)	Symmetry
	No C—H···O interactions possible					
Unsubstituted (II)	C(2)—H	1.00	2.76	3.33	116	$x-1, \frac{1}{2}-y, z-\frac{1}{2}$
	C(3)—H	1.00	2.50	3.20	127	$x-1, \frac{1}{2}-y, z-\frac{1}{2}$
	C(12)—H	1.00	2.70	3.69	173	$1-x, -y, -z$
	C(16*D*)—H2	1.05	2.85	3.69	141	$x, y-1, z$
	C(16*E*)—H2	1.05	2.81	3.38	116	$1-x, 1-y, -z$
1-Methyl (III)	C(2)—H	1.00	2.43	3.34	150	$1-x, y-\frac{1}{2}, \frac{3}{2}-z$
	C(4)—H	1.00	2.73	3.62	148	$x-\frac{1}{2}, \frac{1}{2}-y, 1-z$
	C(6)—H	1.00	2.76	3.64	148	$x-\frac{1}{2}, \frac{1}{2}-y, 1-z$
	C(18)—H1	1.05	2.97	3.55	115	$x, \frac{1}{2}-y, \frac{1}{2}+z$
2-Methyl (IV)	C(3)—H	1.00	2.56	3.53	163	$1+x, \frac{3}{2}-y, \frac{1}{2}+z$
(*a*)	C(15)—H2	1.05	2.93	3.76	140	$x, \frac{3}{2}-y, z-\frac{1}{2}$
	C(18)—H2	1.05	2.97	3.99	176	$1-x, 1-y, 1-z$
	C(18)—H1	1.05	2.59	3.53	153	$x, \frac{3}{2}-y, z-\frac{1}{2}$
6-Methyl (V)	C(2)—H	1.00	2.93	3.52	118	$x, \frac{5}{2}-y, z-\frac{1}{2}$
(*a*)	C(3)—H	1.00	2.65	3.39	130	$x, \frac{5}{2}-y, z-\frac{1}{2}$
	C(12)—H	1.00	2.48	3.46	165	$-x, y-\frac{1}{2}, \frac{1}{2}-z$
	C(16)—H1	1.05	2.62	3.64	164	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
	C(18)—H3	1.05	2.67	3.66	157	$x, \frac{3}{2}-y, z-\frac{1}{2}$
7-Methyl (VI)	C(1)—H	1.00	2.63	3.54	152	$-x, y-\frac{1}{2}, \frac{1}{2}-z$
(*a*)	C(11)—H	1.00	2.42	3.34	153	$-x, y-\frac{1}{2}, \frac{1}{2}-z$
	C(15)—H2	1.05	2.71	3.71	160	$-x, \frac{1}{2}-y, z-\frac{1}{2}$
	C(18)—H1	1.05	2.82	3.62	132	$x, \frac{1}{2}-y, z-\frac{1}{2}$
11-Methyl (VII)	C(2)—H	1.00	3.03	3.89	144	$x, y-\frac{1}{2}, \frac{3}{2}-z$
	C(3)—H	1.00	2.88	3.74	145	$\frac{1}{2}-x, y-\frac{1}{2}, 2-z$
	C(7)—H	1.00	2.47	3.31	141	$x-\frac{1}{2}, -y, \frac{3}{2}-z$
	C(15)—H2	1.05	2.96	3.53	115	$\frac{3}{2}-x, y, z-\frac{1}{2}$
	C(16)—H1	1.05	2.92	3.91	158	$\frac{3}{2}-x, y, \frac{1}{2}+z$
12-Methyl (VIII)	C(4)—H	1.00	2.45	3.44	167	$\frac{1}{2}-x, -y, \frac{1}{2}+z$
(*a*)	C(6)—H	1.00	3.10	3.93	141	$\frac{1}{2}-x, -y, \frac{1}{2}+z$
	C(15)—H2	1.05	3.04	3.73	124	$\frac{1}{2}+x, y, \frac{1}{2}-z$
	C(16)—H1	1.05	2.50	3.44	149	$\frac{1}{2}+x, y, \frac{1}{2}-z$
1,11-Methano (IX)	C(2)—H	1.00	2.51	3.28	133	$\frac{1}{2}-x, -y, z-\frac{1}{2}$
	C(60—H	1.00	2.62	3.48	145	$-x, y-\frac{1}{2}, \frac{1}{2}-z$
	C(18)—H2	1.05	2.85	3.61	129	$\frac{1}{2}+x, y, \frac{1}{2}-z$
7,11-Dimethyl (X)	C(3)—H	1.00	2.54	3.45	151	$x-1, \frac{3}{2}-y, \frac{1}{2}+z$
(*a*)	C(6)—H	1.00	2.67	3.64	164	$x, \frac{3}{2}-y, \frac{1}{2}+z$
	C(15)—H2	1.05	2.63	3.38	128	$x, \frac{3}{2}-y, z-\frac{1}{2}$
	C(16)—H2	1.05	2.78	3.81	166	$x-\frac{1}{2}, y-\frac{1}{2}, \frac{1}{2}-z$
11,12-Dimethyl (XI)	C(4)—H	1.00	2.54	3.40	145	$x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$
	C(16)—H2	1.05	2.51	3.47	152	$-x, 1-y, 1-z$
11-Ethyl (XII)	C(2)—H	1.00	2.38	3.36	165	$1-x, \frac{1}{2}+y, z-\frac{1}{2}$
form (1) *Pnaa*	C(4)—H	1.00	2.82	3.74	148	$\frac{1}{2}+x, \frac{1}{2}-y, z$
	C(6)—H	1.00	2.91	3.81	157	$\frac{1}{2}+x, \frac{1}{2}-y, z$
	C(18)—H	1.05	2.98	3.95	171	$x, \frac{1}{2}-y, \frac{3}{2}-z$
11-Ethyl (XIII)	C(2)—H	1.00	2.47	3.34	149	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
form (2) *Pbca*	C(4)—H	1.00	2.85	3.82	167	$\frac{1}{2}+x, \frac{1}{2}-y, -z$
	C(16)—H2	1.05	2.77	3.72	148	$1-x, 1-y, z$
	C(18)—H1	1.05	2.78	3.53	123	$x, \frac{1}{2}-y, \frac{1}{2}+z$
	C(19)—H3	1.05	2.84	3.75	140	$x, \frac{1}{2}-y, z-\frac{1}{2}$
11-Methoxy (XIV)	C(4)—H	1.00	2.89	3.76	145	$\frac{1}{4}+x, y-\frac{1}{4}, \frac{1}{2}-z$
	C(6)—H	1.00	2.42	3.39	164	$\frac{1}{4}+x, y-\frac{1}{4}, \frac{1}{2}-z$
	C(16)—H1	1.05	2.86	3.53	122	$x, \frac{3}{4}-y, \frac{3}{4}-z$
(*b*)	C(1)—H	1.21	1.98	2.71	114	x, y, z
11-Methyl-11,12-dihydro (XV)	C(6)—H	1.00	2.61	3.59	170	$x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$
	C(15)—H1	1.05	2.84	3.50	121	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
	C(16)—H1	1.05	2.48	3.30	135	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$

Notes: (*a*) There are other C—H···O contacts, only slightly longer, in which all the H atoms define a 'hydrogen pocket' into which the carbonyl oxygen fits effectively. (*b*) Intramolecular hydrogen bond involving the methoxy oxygen; the refined positional coordinates of H are used.

* H at calculated positions.

bonded dimer is nearly planar in the unsubstituted compound (II), it causes a 'step motif' in the 11,12-compound. This is because the C—H···O hydrogen bonding in the 11,12-compound involves a methylene rather than an aromatic H atom and therefore the two molecules in the dimers are at different heights (see Fig. 7). Inspection of Fig. 7 shows that the 'dimer-herringbone' structure is characterized by distinct hydrophilic (C—H···O) and hydrophobic (van der Waals) regions.

The second structural type is exhibited by the high-melting 2-methyl (IV) and 12-methyl (VIII) derivatives. Unlike the 'dimer-herringbone' structure type, this 'high-melting' structure type is not characterized by hydrophilic and hydrophobic regions. Rather, there is a continuous network of branched C—H···O bonds (Fig. 8) which are of the 'stepped' variety in the 2-methyl derivative so that C—H···O bonds effectively link inversion-related molecules. In this way an efficient three-dimensional network is formed. This 'stepped' motif seems to be preferred to the 'planar-dimer' motif, probably primarily for steric reasons, and these features are illustrated in Fig. 8. The crystal structure of the 12-methyl derivative (*Pbca*) appears to be the orthorhombic variation of the monoclinic ($P2_1/c$) structure of the 2-methyl compound. C—H···O bonding, however, now links screw- and glide-related molecules, rather than those related by an inversion centre in the monoclinic structure. Molecules form corrugated ribbons that

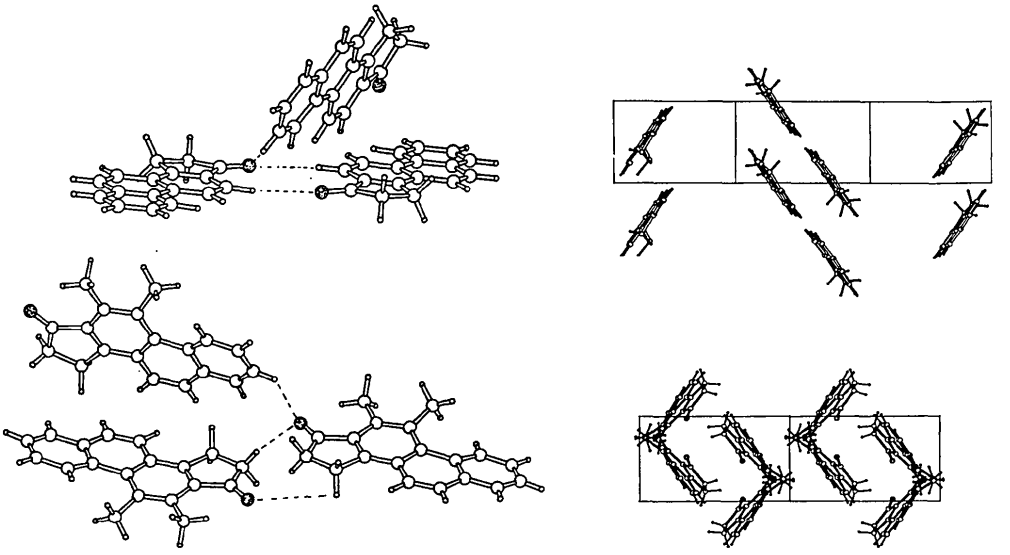


Fig. 7. Interactions in the unsubstituted derivative (above) and the 11,12-dimethyl derivative (below).

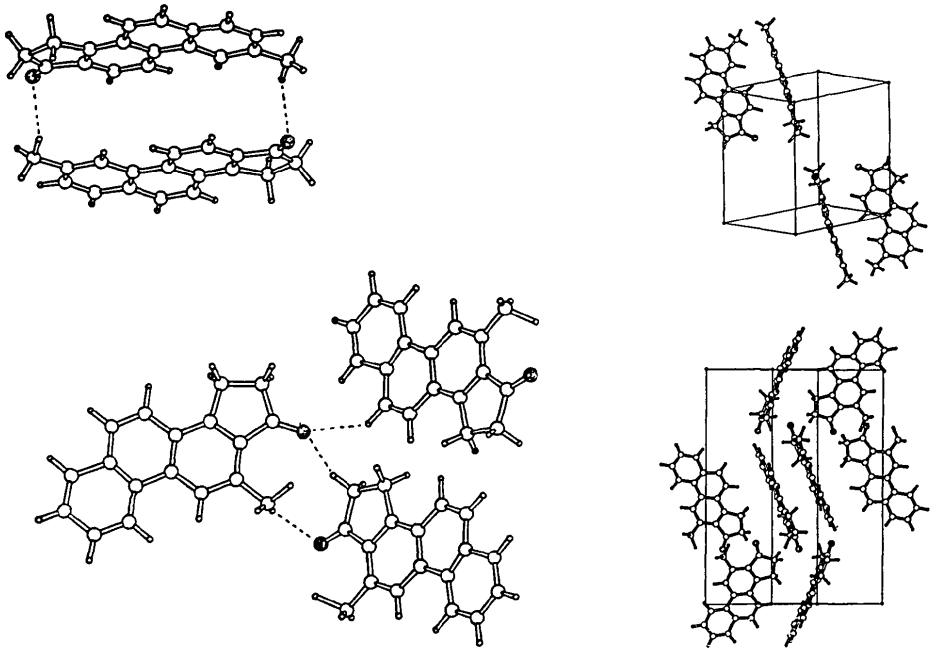


Fig. 8. Interactions in the 2-methyl derivative (above) and the 12-methyl derivative (below).

are stacked along the **a** × **b** direction (~14 Å), as shown in Fig. 8, and this can therefore also be considered, in a sense, as a layer structure.

The most common structure, the third type, is characterized by layers of molecules which are inversion-stacked to generate a crystallographic axis of about 7.5–7.6 Å. This structure is exhibited by the 1-Me, 6-Me, 7-Me, 11-Me, 1,11-methano, 7,11-diMe and both polymorphs of the 11-Et derivative. The 11-MeO derivative (space group *Fddd*) may also be considered a variation of the same structure, being layered, but the axis perpendicular to the layers is now doubled to 13.823 Å. Therefore, there are four layers of molecules in the unit cell. The molecule is planar and the intermolecular distance (13.823/4 = 3.456 Å) is close to the van der Waals stacking distance. The C—H···O motifs found within the layers are typified in Fig. 9, and the structures may be considered to be built up by a van der Waals stacking of such C—H···O bonded layers. The stacking patterns are inversion- rather than translation-related (since the axes are 7.5 Å rather than ~3.8 Å), probably for steric and electronic reasons (Sarma & Desiraju, 1986; Desiraju & Kishan, 1989). In the 6-Me derivative the molecules are arranged in ribbons rather than in stacks, and inclined ribbons are connected by C—H···O hydrogen bonds. The stacking of ribbons is, however, across inversion centers, as shown in Fig. 10. The crystal structure of the 6-methyl derivative is therefore equivalent to the other members of the group.

The planarity of the 11-methoxy derivative suggests that this intramolecular interaction is attractive. In the 11-ethyl and 11-methyl derivatives, where such an interaction is not attractive, the torsion angles are 8.9 and 13.3° for the two polymorphs of the 11-ethyl derivative and 13.5° for the 11-methyl derivative. If there were a van der Waals repulsion between the hydrogen [H(1)] and oxygen [O(11)], then the methoxy group should be twisted (which it is not).

The three types of stacking patterns described here are different from those of polycyclic aromatic hydrocarbons which, if large, can stack with a translation of 4 Å. The dihydrocyclopentaphenanthrenes do not stack in this way, an observation that can be attributed to the bulk of the methylene and methyl groups and to the dipole moment of the carbonyl group. Some of the stacking modes are shown in Fig. 11. These show the twofold relationship of molecules in the 11-methoxy (*Fddd*) and 11-ethyl (*Pnaa*) crystal structures and the *c*-glide relationship in the 7,11-dimethyl ($P2_1cn$) and 11-methyl (*Pcab*) crystal structures.

These studies highlight the importance of C—H···O networks in establishing molecular packing in crystals of substituted aromatic oxohydrocarbons even when the relative oxygen stoichiometries are low. The effects may be electrostatic (Klooster, Swaminathan, Nanni & Craven, 1992) since H atoms in polycyclic aromatic hydrocarbons have a small positive charge (Klein *et al.*, 1987). These C—H···O interactions warrant further study. Although O—H···O networks have been used

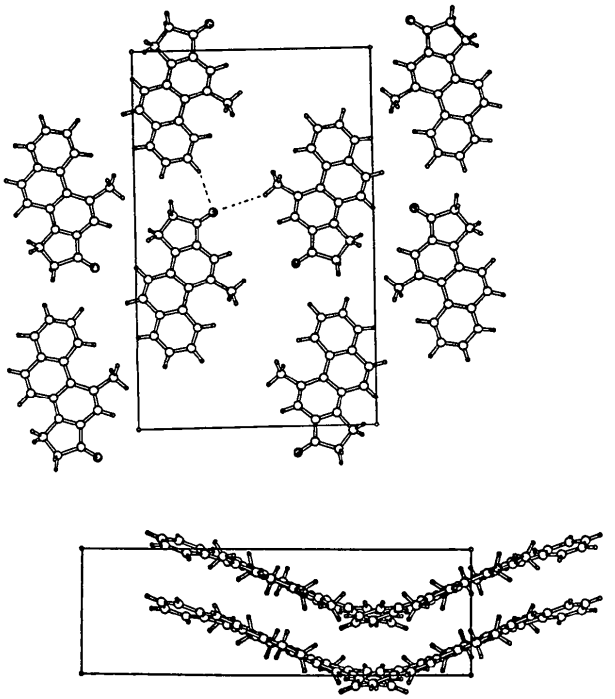


Fig. 9. Interactions in the 11-methyl derivative showing (above) only one layer of molecules and (below) the herringbone arrangement of the molecules.

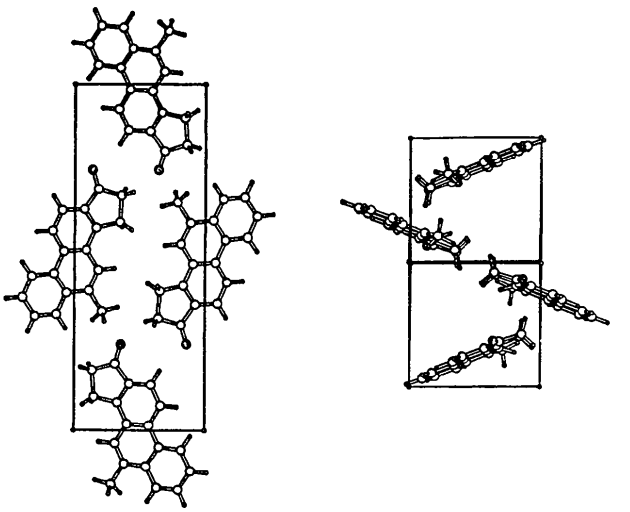


Fig. 10. Packing in the 6-methyl derivative.

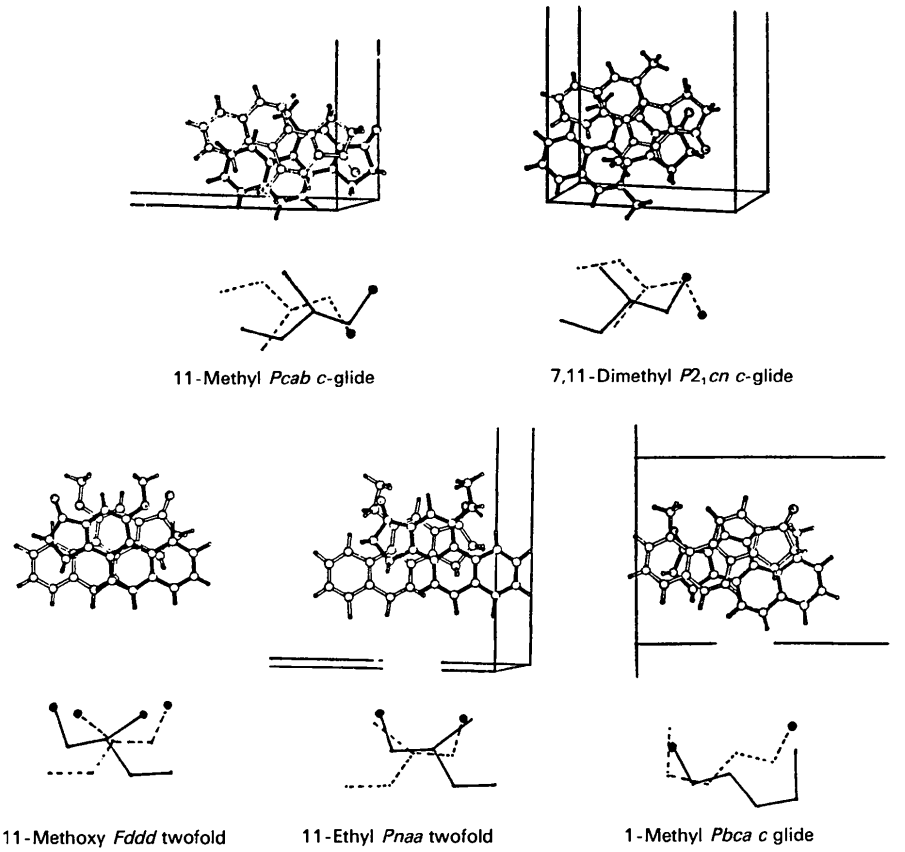


Fig. 11. Some stacking modes.

to predict secondary and tertiary structures of macromolecules, the very weakness of C—H···O interactions has discouraged investigators from exploring analogous networks in the more hydrophobic interiors of macromolecules. The trends observed in this study may aid in such model building.

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Structure of a Cyclophane Host Molecule

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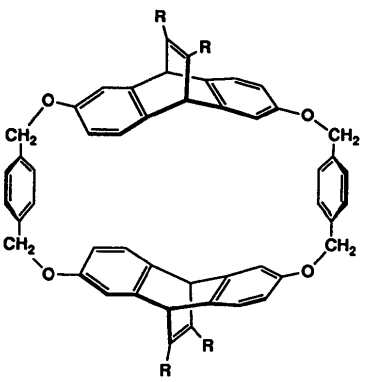
Abstract

The cyclophane tetramethyl 3,8,13,18a,21,26,31,36a-octahydro-4,6:9,12:22,24:27,30-tetraetheno-15,18,21:-33,36,39-diethenylylidenedibenzo[*k*,*a*1][1,8,17,24]-tetraoxacyclodotriacontene-1,2,19,20-tetracarboxylate acetonitrile solvate, $C_{56}H_{44}O_{12}.CH_3C{\equiv}N$, contains a large cavity and forms host–guest complexes in solution with a variety of quaternary nitrogen compounds. Crystallization from an acetonitrile solution that contained adamantyltrimethylammonium iodide led, though, to crystals of the uncomplexed cyclophane (but containing one molecule of acetonitrile of crystallization). The cavity, about 7.6 × 4.0 Å and roughly rectangular in cross section, is occupied by ester groupings from two adjacent cyclophanes, entering from opposite sides. Crystal data: orthorhombic, $P2_12_12_1$, with $a = 11.741$ (6), $b = 16.155$ (5), $c = 25.895$ (7) Å, $V = 4912$ Å^3, $T = 296$ K, $Z = 4$, $M_r = 950.01$, $D_x = 1.28$ g cm^{-3}, $F(000) = 1992$, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.84$ cm^{-1}, $R = 0.0538$ for 2410 independent reflections with $I > 0$, $S = 2.29$ for 2610 total reflections.

Introduction

Cyclophane (I) and its tetracarboxylate derivative (II) (Fig. 1) have been studied extensively as hosts for a variety of guests. In water, the tetraanion (II) is a powerful receptor for a wide array of structures (Petti, Shepodd, Barrans & Dougherty, 1988). Most notable is the ability of (II) to tightly bind quaternary ammonium and imminium compounds through the 'cation–π' interaction. This novel binding force results from the positive charge of a guest being stabilized by direct contact with the electron-rich faces of the aromatic rings that form the walls of the receptor. Tetraester (I) serves as an efficient host for appropriate cation guests in organic media (Stauffer & Dougherty, 1988). These studies have led to a new model for the binding of the important neurotransmitter acetylcholine (Dougherty & Stauffer, 1990).

Cyclophanes (I) and (II) were designed to be fairly rigid structures with the six aromatic rings forming the walls of a central cavity. Modelling studies show



(I) R = CO_2Me

(II) R = $CO_2^-Cs^+$

Fig. 1. A schematic drawing of the cyclophane (I) and its tetracarboxylate derivative (II).

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